A STUDY OF THE CATALYTIC DECOMPOSITION OF UREA

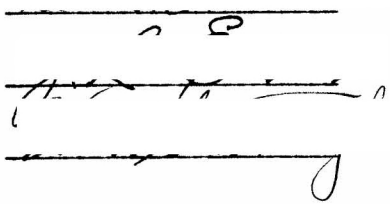
A thesis submitted
in partial fulfillment
of the requirements for the degree
of Master of Science
in Chemistry

by

Lloyd E. Parks

Georgia School of Technology
Atlanta, Georgia
1940

Approved by:



ACKNOWLEDGEMENTS

The author wishes to express his appreciation and thanks to Dr. W. S. Taylor, both for the suggestion of this problem, and for his timely advice throughout the course of the work.

L.E.P.

TABLE OF CONTENTS

FOREWORD

The purpose of this investigation has been to study the catalytic decomposition of urea in an attempt to obtain hydrogen, nitrogen, and carbon monoxide as decomposition products. It was undertaken with the idea that such a reaction, with the same catalyst under different conditions, might be reversed to yield urea directly from hydrogen, nitrogen, and carbon monoxide. Such a synthesis of urea should be cheaper than the one used at the present time. The reaction is thermodynamically possible as indicated by its negative free energy change, and is favored by the tremendous volume change.

The general approach was to decompose urea in the presence of various metals and metal oxides under varied conditions and to test qualitatively the gaseous decomposition products.

A STUDY OF THE
CATALYTIC DECOMPOSITION OF UREA

HISTORICAL

Urea was first definitely isolated by Fourcroy and Vauquelin, (1) and reported in two papers on, "The Constituents of Urine", in 1799 and 1800. For a quarter of a century, thereafter, the only source of urea was urine; consequently, much work was done in effecting methods of extraction and purification.

In 1828 Wohler did what was thought to be the impossible, by synthesizing urea, an organic compound, from the inorganic constituents cyanic acid and ammonia:

$$NH_3 + HOCN \longrightarrow NH_4OCN \longrightarrow OC(NH_2)_2.$$

This discovery altered the whole outlook of chemistry. Organic chemistry dates from it in two respects; it broke down the old Vital Force theory which was a barrier between organic and inorganic chemistry, and was the first sample of organic synthesis.

Since the time of Wohler's discovery, a great number of processes have been developed for the synthesis of urea, but only two are of any great commercial importance. They are,

---

(1) Fourcroy and Vauquelin; Annales de Chimie, xxxi, 49 (1799), and xxxii, 80 (1800).

briefly:

(1) The direct union of ammonia and carbon dioxide,

$$2\,NH_3 + CO_2 \longrightarrow OC(NH_2)_2 + H_2O;$$ and

(2) The hydration of cyanamide,

$$NH_2\text{-}C\,N + H_2O \rightleftharpoons NH_2\text{-}\underset{OH}{C}NH \rightleftharpoons NH_2\text{-}CO\text{-}NH_2.$$

The first and most important of the two processes consists of passing a mixture of ammonia and carbon dioxide, with some moisture, into an autoclave at 130° to 140° C; ammonium carbamate ($NH_2.CO.ONH_4$) forms first and is transformed into urea by the loss of a molecule of water:

$$2\,NH_3 + CO_2 \longrightarrow NH_2.CO.ONH_4,$$ and

$$NH_2.CO.ONH_4 \longrightarrow NH_2.CO.NH_2 + H_2O$$

A 40 per cent conversion is effected and the excess ammonia and carbon dioxide is recovered and used again.

PURPOSE AND SCOPE OF INVESTIGATION

Urea has a high percentage of nitrogen and could be used more extensively as a fertilizer if it were not for the fact that it is so expensive, $95.00 per ton. A comparison of the free energy change for the formation of urea in the reaction representing the present commercial synthesis,

$$(1)\ 2\ NH_3 + CO_2 \longrightarrow OC(NH_2)_2 + H_2O \quad ; \quad \Delta F = \quad -1{,}600 \text{ cal.}$$

with that of the free energy change in the following reaction,

$$(2)\ 2\ H_2 + N_2 + CO \longrightarrow OC(NH_2)_2 \quad ; \quad \Delta F = \quad -14{,}610 \text{ cal.}$$

shows that reaction (2) has a greater negative free energy change than reaction (1). This indicates that reaction (2) is thermodynamically possible, and should have a greater tendency to take place than reaction (1) if the right catalyst and conditions could be found. A study of equation (2) shows that four volumes of gases unite to form one volume of urea. This large decrease in volume would greatly favor the desired reaction.

The materials for the synthesis would be cheap since carbon monoxide and hydrogen can be obtained from water gas and nitrogen can be obtained from air.

The method of attack chosen for this problem was to study the catalytic decomposition of urea in an attempt to find a catalyst that would alter the ordinary thermal decomposition to

produce hydrogen, nitrogen, and carbon monoxide. Such a catalyst under different conditions of temperature and pressure would favor the reversal of the decomposition to form urea as indicated by the negative free energy change and volume change.

Normally urea dissociates (1) just above its melting point (132°), to yield ammonia and an equilibrium mixture of the cyanic acids;

$$HNCO \rightleftharpoons HOCN$$

which may react with unchanged urea to form biuret;

$$HNCO + OC(NH_2)_2 \longrightarrow NH(CONH_2)_2.$$

Biuret decomposes on further heating to give tricyanourea $(NH_2\text{-}CO\text{-}NHCN)_3$. When urea is heated under reduced pressures a sublimate of ammonium cyanate (NH_4NCO) is obtained.

(1) Hurd, C. D.; Pyrolysis of Carbon Compounds, The Chemical Catalog Company, Inc., New York, 1929, p. 604.

EXPERIMENTAL

PRELIMINARY TESTS

(a) A Study of the catalytic effect of various metals and metal oxides.

Four grams of dry urea were thoroughly mixed, in a mortar, with approximately one gram of the metal or metal oxide under consideration. The mixture was placed in a test tube and heated. The gaseous decomposition products were passed; first through water containing phenolphthalein to detect and remove any ammonia formed, and then through an ammoniacal silver solution. The test tube was heated in an oil bath and the temperature at which the phenolphthalein turned red was recorded as that at which ammonia was liberated. The presence of reducing gases, carbon monoxide or hydrogen would be indicated by the precipitation of black metallic silver from the silver solution.

The results obtained are tabulated in Table I on the following page:

Table I. Results from the decomposition of small samples of urea in the presence of metals and metal oxides.

Metal or Oxide used	Temp. of Ammonia Liberation (degrees centigrade)	Presence of Reducing Gas
Al_2O_3	223	Negative
As_2O_3	249	"
CoO	210	"
Cr_2O_3	216	"
CuO	237	"
Fe_2O_3	219	"
MnO_2	213	"
NiO	172	"
PbO_2	280	"
Sb_2O_3	249	"
SnO	194	"
UO_3	204	"
ZnO	233	"
ZrO	247	"
Cu	230	"
Fe	208	"
Ni	177	"
Pb	275	"
Sn	194	"
Zn(course)	203	"
Zn(finely divided)	190	"
Pure Urea	150	"

Ammonia is known to be the first gaseous decomposition product of urea; consequently, the temperature at which it is first liberated might be a qualitative indication concerning the catalytic effect of the metal or oxide used.

The ammoniacal silver solution used in the test for reducing gases was prepared as follows (1): 1.7 grams of silver nitrate were dissolved in water; to this solution, 36 cc. of 10 per cent ammonia and 160 cc. of 10 per cent sodium hydroxide were added and the volume made up to 1 liter. This solution is especially sensitive to carbon monoxide and can be used in the presence of hydrogen. According to the literature, (1) traces of carbon monoxide as small as 0.06 per cent will reduce enough silver to give a precipitate in one minute. Higher percentages of carbon monoxide yield a heavy precipitate almost instantly. The results of our tests with known samples of hydrogen and carbon monoxide check those indicated above, in a qualitative way, and indicate that hydrogen will yield a slight precipitate after several minutes.

The only conclusion that could be drawn from these preliminary tests was that the substance used did not yield a reducing gas, and that they acted as negative catalysts or retarded the normal decomposition of urea. Nickel and its oxide showed the least negative catalytic effect; consequently, they were chosen for further study.

(1) Lunge, G.; Technical Gas Analysis, (Revised by H. R. Ambler), Gurney and Jackson Co., London, 1934, p. 228.

(b) Nickel as a catalyst.

(1) To study the effect of the state of subdivision of the catalyst.

Samples of finely divided nickel were prepared as follows: A solution of nickel nitrate was thoroughly mixed in a mortar, and slowly added to a solution of the calculated amount of ammonium carbonate to form the nickel carbonate. The resulting mixture was filtered, washed, and allowed to dry for 10 hours at 110° C. Just before use a small amount of the product was reduced for one hour at 400° C. in a stream of hydrogen. The catalyst was then cooled to room temperature in an atmosphere of hydrogen and transferred to the reaction tube which contained urea in an atmosphere of carbon dioxide. The contents of the tube were thoroughly mixed and the decomposition was carried out under reduced pressure.

The gaseous products were tested as previously. No reducing gas was detected, and the temperatures at which ammonia was evolved did not vary appreciably from that reported in the previous tests.

These tests led to the conclusion that no catalytic action took place below the temperature at which normal thermal decomposition occurred.

(2) A Study of the effect of temperature on the catalytic decomposition.

Since urea decomposes before catalytic action starts, an effort was made to bring urea or its vapors into contact with the preheated catalyst. According to the literature, (1) urea can be distilled under reduced pressure. Based on this statement, an attempt was made to distill urea, under reduced pressure, over the finely divided preheated nickel catalyst. The catalyst was prepared as previously described, using asbestos as a base, and placed in a tube surrounded by a heating element.

All attempts to distill the urea over the catalyst at reduced pressures failed. Subsequent efforts to distill urea under pressures as low as 8mm were unsuccessful. A slight sublimation took place which appeared to be due to the formation of some ammonium cyanate, an ordinary decomposition product which sublimes at about 160°-180° C. in a vacuum. The melting point of this sublimate was checked on several runs to prove that it was not urea. No reducing gas was detected.

(1) Butka, H. E. and Meisner; J. Lab. Clin: Med. 10, 937 (1935).

RAPID DECOMPOSITION OF UREA ON PREHEATED SURFACES

(a) Development of process.

Urea vapors could not be passed over the preheated catalyst; so the only alternative was to drop the solid or molten urea on the hot catalyst. Preliminary tests were carried out by dropping urea on molten lead. A rapid evolution of gases resulted and subsequent tests showed that some of these gases were of a reducing nature. Great difficulty was encountered in designing satisfactory apparatus for carrying out this type reaction and collecting the decomposition products.

The first idea was to draw molten urea through molten lead. This was accomplished by reducing the pressure with an aspirator, and at the same time the gases were drawn through the test solutions. The presence of a reducing gas was indicated by a slight precipitation of silver in the ammoniacal silver solution.

The next problem was to over-come the difficulties encountered in the process, and to collect and analyze sufficient quantities of the gases to represent the true decomposition products. It was observed that enough air was passing through the system to oxidize the lead, very rapidly, to lead oxide. This had to be over-come in order to prevent reaction between the hot oxide and reducing gases formed in the decomposition of the urea. Another serious

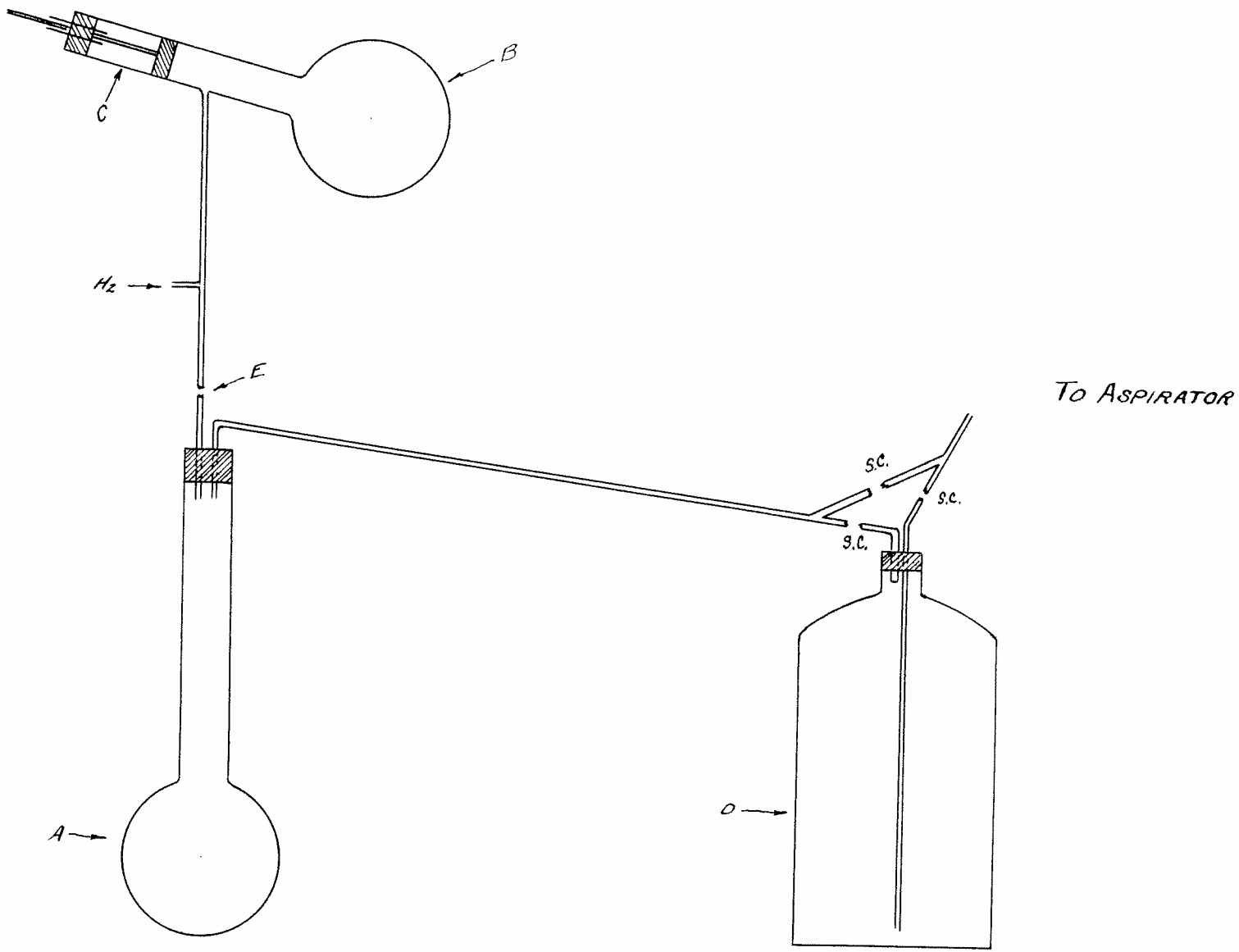
difficulty was encountered in drawing the molten urea through the tube beneath the surface of the molten lead. The decomposition products of the urea had a tendency to solidify in the tube, just above the surface of the hot lead, and closed it up. To over-come this last difficulty, solid urea was dropped on the surface of the molten lead.

The following proceedure, and the set-up on the following page was the most satisfactory:

General proceedure: Approximately 450 grams of granulated lead was placed in the Kjeldahl flask, A; a weighed amount of dry urea in the bulb, B, of a 125 cc distilling flask; and ten grams of urea in compartment, C, of the flask. Bottle, D, was filled with a weak solution of H_2SO_4 to remove any ammonia liberated.

Hydrogen was passed through the system for about an hour, until all oxygen was removed, before the lead was heated. The system was tested for leaks and the hydrogen generator removed. The lead was heated just above its melting point and the urea from compartment, C, was allowed to drop on the surface of the molten lead by manipulating the plunger in the neck of the distilling flask. The purpose of the pinch-cock, E, was to regulate the rate of adding urea. Every effort was made to clear the system of residual hydrogen as the first ten grams of urea were decomposed over a period of 30 to 45 minutes. During this time the gases were drawn directly into the aspirator. Finally the decomposition gases from a weighed sample of urea were collected in the bottle and analyzed.

Apparatus For The Decomposition of Urea



A considerable amount of white solid substance condensed on the walls of the flask. This substance was perhaps ammonium cyanate, but no attempt was made to actually identify it since we were interested primarily in the gaseous decomposition products. There was no indication of the formation of lead oxide or carbon.

(b) Analytical results.

Samples of the gases exploded, when tested with a flame, in a manner suggestive of hydrogen. The presence of hydrogen and nitrogen was to be expected since ammonia breaks down to yield both of these elements when it is heated to high temperatures.

Samples of the gases were drawn through the ammoniacal silver solution and a slight precipitate formed indicative of the presence of a reducing gas. From the small amount of precipitate and the slow rate of precipitation, it was concluded that only a trace, if any, carbon monoxide was present and that the reducing gas was hydrogen.

At this point it was considered advisable to resort to the standard Orsat apparatus for a more thorough analysis of the gases. The decomposition was accomplished on different hot surfaces, and the gaseous products collected as outlined previously.

The general outline of the Orsat method of volumetric gas analysis is as follows:

(1) Carbon dioxide is absorbed in a solution of KOH,

(2) Oxygen is absorbed in alkaline pyrogallol,

(3) Unsaturated hydrocarbons are absorbed in fuming sulfuric acid.

(4) Hydrogen and carbon monoxide are oxidized to water and carbon dioxide by copper oxide at 325 degrees (volume change is hydrogen)

(5) Carbon dioxide formed above is absorbed in KOH solution and the volume change is carbon monoxide,

(6) Saturated hydrocarbons are burned in a combustion chamber in the presence of oxygen and the percentages calculated, and

(7) Residual gas is nitrogen.

The results of the Orsat determinations were as follows:

Determination I.

Eight grams of urea were decomposed on the surface of pure lead. Ammonia and carbon dioxide were absorbed in sulfuric acid and potassium hydroxide before the gases were collected. 800 cc. of gases collected. 100 cc. sample tested.

CO_2 --- none

CO --- none

O_2 --- 14.4%

H_2 --- 31.6 %

N_2 --- 54.0 %

Unsaturated hydrocarbons --- none

Saturated hydrocarbons --- none

Determination II.

Five grams of urea were decomposed on the surface of lead containing a small quantity of nickel. Ammonia and carbon dioxide were absorbed before the gases were collected. 800 cc. of gases collected. 100 cc. sample tested.

CO_2 --- none

CO --- none

O_2 --- 6.1 %

H_2 --- 68.4 %

N_2 --- 25.5 %

Unsaturated hydrocarbons --- none

Saturated hydrocarbons --- none

Determination III.

Ten grams of urea were decomposed on the surface of lead containing a small quantity of nickel. In this case the carbon

dioxide was not removed. Ammonia was absorbed before gases were collected. 1100 cc. of gases were collected. 100 cc. sample tested.

CO_2	--- 0.4 %	H_2	--- 47.0 %
CO	--- none	N_2	--- 43.0 %
O_2	--- 9.6 %		

Unsaturated hydrocarbons --- none

Saturated hydrocarbons --- none

Determination IV.

Urea decomposed on the surface of hot glass (temperature kept as near that of the melting point of lead as possible). Ammonia and carbon dioxide absorbed before the gases were collected.

CO_2	--- none	H_2	--- 49.6 %
CO	--- none	N_2	--- 41.4 %
O_2	--- 9.0 %		

Unsaturated hydrocarbons --- none

Saturated hydrocarbons --- none

As indicated above, the residual gas in the Orsat determination was nitrogen. This was was proven to be nitrogen by passing it over hot magnesium to form the nitride and hydrolyzing to form ammonia.

These tests show, in a qualitative way, that hydrogen and nitrogen can be obtained by decomposing urea on hot surfaces. This is to be expected since ammonia yields both elements when subjected to high temperatures. The values are of little quantitative value since hydrogen was used to sweep the system free of oxygen before the decomposition was carried out.

The fact that hydrogen was used to sweep the system free from air at the beginning of the process most probably accounts for the discrepancy in the percentages of hydrogen as reported in Determinations I and II. Incorrect percentages of hydrogen would lead directly to incorrect percentages of nitrogen. We were not interested, especially, in the quantitative analysis of these gases.

It is rather hard to explain the formation of oxygen in the presence of hydrogen, but every effort was made to keep atmospheric oxygen from the system, consequently, it must have been one of the products of decomposition of urea. The amount of carbon dioxide formed was almost negligible; but its presence might be expected since, in the presence of moisture, urea will decompose to yield carbon dioxide. The solid residue which was left in the flask was not analyzed.

Negative tests for carbon monoxide were obtained, both by the sensitive ammoniacal silver solution and by the Orsat determinations; so all efforts up to the present time have failed to yield carbon monoxide as one of the decomposition products of urea.

Time did not permit a detailed study of the effect of different hot catalytic surfaces at different temperatures on the decomposition of urea.

CONCLUSION

All attempts to find a catalyst for the decomposition of urea into hydrogen, nitrogen, and carbon monoxide were unsuccessful. The most promising method of decomposition developed consisted of dropping solid urea on the preheated catalytic surface. Even in this case, the desired results were not obtained under the conditions of temperature used and with the catalysts studied.